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Infrared E-type band shapes of the liquid CD_3I and CD_3CN: Orientational diffusion and free rotation

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Abstract

Infrared absorption spectra of liquid methyl iodide-d_3 (CD_3I) and acetonitrile-d_3 (CD_3CN) have been studied in wide temperature ranges (212–317 K and 234–346 K, respectively). IR spectra in the regions of degenerate (E-type) bands belonging to CD_3-stretching and deformational vibrations (ν_4, ν_5, ν_6 of CD_3I and ν_6, ν_7 of CD_3CN) were fitted by the sum of Cauchy-Gauss components. Each E-type band was reproduced by the sum of two components: the narrower (n) and the broader (b) ones. The different temperature behaviour of the components has been found: the integrated intensities of the narrower components (I_n) decrease with the temperature, while the intensities of the broader ones (I_b) increase. The narrower components of the bands belonging to deformational CD_3-vibrations were interpreted within the framework of the orientational diffusion mechanism. The broader components of these bands were attributed to the unresolved gas-like vibration-rotational absorption of the molecules. The enthalpy differences between the molecules absorbing via two different mechanisms (ΔH) were determined from the dependencies of $\ln(I_n/I_b)$ upon T^{-1}: 0.59 ± 0.15 (CD_3I) and 1.10 ± 0.20 koal mol^{-1} (CD_3CN). These values are close to those determined previously for nondeuterated methyl iodide and acetonitrile, respectively. The shape of the CD_3-stretching E-type band of CD_3I is assumed to be mainly due to interactions of the C–D stretching vibrations with single particle and collective motions of molecular dipoles. An attempt is made to separate the widths of the narrower components into the contributions of orientational and vibrational relaxation. Various experimental and theoretical approaches to molecular relaxation are considered in view of the obtained data.

Keywords: Orientational diffusion; Free rotation; Acetonitrile; Methyl iodide; Vibrational relaxation; Infrared spectra

1. Introduction

The rotation of several small molecules or small molecular fragments in liquid inert media is considered to be nearly free. This means that the spectra of the systems under study contain the features of the free rotation. Thus, mid-infrared (IR) spectra of the hydrogen halogenides (HCl, HBr, HI and HF) dissolved in alkanes, benzene, carbon disulfide, haloforms and liquefied noble gases represent the wings which are similar to the vapour-phase spectra [1–5]. Other examples are CO and NO dissolved in CCl_4, $SnCl_4$ [1] and

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